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COMPLETE SPECIFICATION

Process for Polymerization and the products produced thereby

We, AMERICAN CYNAMID COMPANY, a corporation organised under the laws of the State of Maine, United States of America, of 30, Rockefeller Plaza, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing graft polymers comprising polymerizing a polymerizable monomeric compound and containing a polymerizable $\text{CH}_2=\text{C}<$ group in an aqueous medium at a pH not greater than 6 and preferably not greater than 3.5 and in the presence of certain polymeric organic reducing agents and a ceric salt which is soluble in at least one component of the reaction system. Still further, this invention relates to an aqueous solvent polymerization process wherein a vinyl or vinylidene monomer, which is at least partially soluble in water, is polymerized in the presence of a ceric salt which is soluble in at least one component of the reaction system wherein the pH of the aqueous medium is maintained at 6 or below. Still further, this invention relates to the process of polymerizing, in an aqueous emulsion, a polymerizable vinyl or vinylidene monomer at a pH not greater than 6, in the presence of a ceric salt which is soluble in at least one component of the reaction system and certain polymeric organic reducing agents. Still further, this invention relates to the graft polymers produced which comprise a substantially pure polymeric inter-reaction product of a polymerizable monomer that contains a polymerizable $\text{CH}_2=\text{C}<$ group and a polymeric organic reducing agent which is capable of being oxidized by said ceric salt which is capable of initiating the polymeriza-

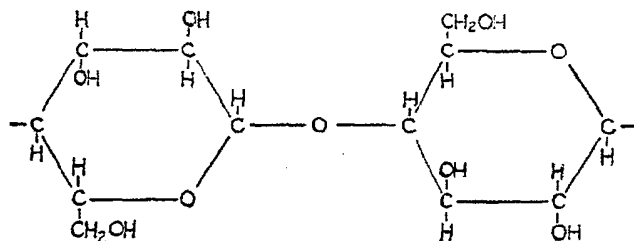
tion, said reducing agent being selected from the group consisting of polymeric alcohols, ketones, mercaptans, amines, aldehydes and acetals.

In accordance with the invention there is provided a process for preparing graft polymers and linear oligo block copolymers comprising polymerizing a polymerizable monomeric compound containing a polymerizable $\text{CH}_2=\text{C}<$ group in an aqueous medium at a pH not greater than 6.0 and at a temperature between -5°C . and 100°C . in the presence of a ceric salt which is soluble in at least one of the components of the reaction system, and a polymeric organic reducing agent which is capable of being oxidized by said ceric salt and which is capable of initiating the polymerization, said agent being an aldehyde or an acetal or a

compound containing the $\begin{array}{c} \text{X} \\ | \\ -\text{C}-\text{H} \end{array}$ group wherein X is OH, RCO, SH and NHR, wherein R is hydrogen, alkyl, aralkyl or aryl,

the open bonds of said $\begin{array}{c} \text{X} \\ | \\ -\text{C}-\text{H} \end{array}$ group being essentially organic residues and/or hydrogen.

The invention also provides a process for preparing graft polymers comprising polymerizing a polymerizable monomeric compound containing a polymerizable $\text{CH}_2=\text{C}<$ group dissolved at least partially in an aqueous medium at a pH not greater than 3.5 in the presence of a ceric salt which is soluble in at least one of the components of the reaction system and a cellulosic material which is capable of being oxidized by said ceric salt and which is capable of initiating the polymerization, said cellulosic material containing the recurring group



or a partial ether or partial ester thereof.

In the practice of the process of the present invention, the polymerization is carried out in aqueous solution or an aqueous emulsion as contrasted with other solvent polymerization processes such as organic solvent polymerization or even bulk polymerization. Inasmuch as the process of the present invention may be carried out in an aqueous solvent medium or in an aqueous emulsion medium, it is immaterial as to whether or not the polymerizable monomeric vinylidene or vinyl compound is water-soluble. If the polymerizable material is completely water soluble, one need not resort to use of an emulsifying system. On the other hand, if the polymerizable monomer is only partly soluble in water, one may find that the polymerization can be carried out in an aqueous solvent medium, without benefit of an emulsifying agent, by means of a dispersing agent or by use of a dispersing technique such as rapid agitation wherein the monomeric material, the reducing agent and the ceric salt have ample opportunity to come into reactive contact with one another to produce the desired polymerization product. For monomeric materials that are only slightly soluble in water or are substantially completely insoluble in water, the emulsion polymerization technique is recommended.

In carrying out the process, it is imperative to use at least one of a class of certain polymeric organic reducing agents as described briefly hereinabove and discussed more fully hereinbelow and a ceric salt which is soluble in at least one of the compounds component of the reaction system, namely for instance, in the vinylidene monomer and/or the polymeric organic reducing agent and/or water.

Among the monomeric polymerizable compounds which may be used in the practice of the process of the present invention are those containing a polymerizable $\text{CH}_2=\text{C}<$ group. This includes vinylidene compounds and/or vinyl compounds. More specifically, the following polymerizable monomers may be used: styrene, and substituted styrenes such as ring-substituted and side-chain substituted styrenes, e.g., α -chlorostyrene, α -methylstyrene, o-methylstyrene, p-methylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, 2,4,5-trimethylstyrene, p-ethylstyrene, o-bromostyrene, 2-bromo-4-ethylstyrene, p-iso-

propylstyrene, p-chlorostyrene, 2,4-dichlorostyrene, or polymerizable acrylic compounds, such as acrylic acid and its homologues such as methacrylic acid, α -chloroacrylic acid and derivatives thereof such as the anhydrides, amides and nitriles, and the acrylic type acid esters of monohydric alcohols such as the methyl, ethyl, propyl, butyl, isobutyl, amyl, hexyl, cyclohexyl, heptyl, octyl, decyl alcohols or the acrylic type acid esters of nitro alcohols such as 3-nitro-2-butanol, 2-nitro-3-hexanol, 2-methyl-2-nitro-1-butanol and 2-nitro-2-methylpropyl alcohol, and the acrylic type acid esters of polyhydric alcohols such as ethylene glycol, diethylene glycol, glycerol, pentaerythritol, dipentaerythritol, propylene glycol, or dipropylene glycol. Additionally, one may make use of such polymerizable monomers such as butadiene, isoprene, and haloprenes such as chloroprene. Still further, as the polymerizable monomer, one may use allyl compounds such as allyl alcohol or allyl or substituted allyl esters such as methallyl esters. More specifically, one may use allyl acetate, allyl propionate, allyl chloroacetate, allyl caproate, allyl linoleate, allyl benzoate, methallyl acetate, the allyl ester of isobutyric acid, allyl acrylate, diallyl carbonate, diallyl oxalate, diallyl phthalate, diallyl maleate, or triallyl cyanurate. Still further, one may make use of the vinyl or vinylidene esters such as vinyl acetate, vinyl chloride, vinylidene chloride, vinyl propionate, or vinyl butyrate. Vinyl ethers may also be used such as vinyl ethyl ether, vinyl propyl ether, or vinyl isobutyl ether or other vinyl compounds such as divinyl sulfone, divinyl sulfide, or vinyl pyridine. Additionally, one may make use of the unsaturated polymerizable amides such as acrylamide, methacrylamide, ethacrylamide, or methylenebisacrylamide, or the nitriles such as acrylonitrile, methacrylonitrile, ethacrylonitrile, or alpha-chloroacrylonitrile. Whenever desirable, these polymerizable monomers may be used either singly or in combination with one another.

In the practice of the present invention, it is imperative that a polymeric organic reducing agent be used which is capable of being oxidized by the ceric salt which is present in the system and which is capable of initiating the polymerization of the compound containing the $\text{CH}_2=\text{C}<$ group.

These reducing agents are compounds con-

taining the $\begin{array}{c} \text{X} \\ | \\ -\text{C}-\text{H} \end{array}$ group wherein X is a

5 member selected from the group consisting of OH, RCO, SH and NHR; wherein R is a member selected from the group consisting of hydrogen, alkyl, aralkyl and aryl. Fundamentally, this description of the class of reducing agents encompasses such classes of compounds as alcohols, or compounds containing an alcoholic hydroxy group, ketones, mercaptans, amines and the like. Additionally, aldehydes can be used, as well as acetals.

The open bonds in the $\begin{array}{c} \text{X} \\ | \\ -\text{C}-\text{H} \end{array}$ compounds

15 are organic residues and/or, in one instance only, hydrogen. Thus, for example, they may be alkyl, both substituted and unsubstituted, aralkyl, both substituted and unsubstituted, or any combination of these groups, or hydrogen, in one instance only. These organic groups or
20 any combination thereof may be substituted or unsubstituted and if substituted, may contain, for instance, such substituent groups as nitro, amino, hydroxyl, carboxyl, carbonyl, halo, alkoxy, alkyl, amino, carboxyl, sulfo,
25 phospho and mercapto groups, individually, in plurality or admixtures thereof.

The reducing agents used in the practice of the process of the present invention are classed as polymeric reducing agents, which
30 term is intended to include dimers, trimers, and higher polymeric materials, both natural and synthetic. These polymeric reducing agents are reactive in the system and become a part of the ultimate polymeric reaction product produced. These reducing agents will
35 constitute backbones or blocks to which the vinylidene and/or vinyl monomer used in the present invention are readily attached to form graft copolymers or linear oligo block copolymers. By oligo block copolymers, as the
40 term is used herein, is meant block copolymers composed of a few blocks of relatively long sequences having a degree of polymerization equal to 50 monomer units or
45 more as opposed to conventional block copolymers formed of a large number of relatively short sequences having a degree of polymerization of less than 50 monomer units joined together through reactive end groups.
50 Among the materials which are effective as preformed polymeric reducing agents adapted for use as backbones or blocks in the formation of graft copolymers or linear oligo block copolymers in accordance with the present
55 invention are compounds containing one or more alcoholic hydroxy groups. Illustrative of this class of polymeric reducing agents are polyvinyl alcohol, partial esters of polyvinyl alcohol, as, for example, formylated poly-

vinyl alcohol, acetylated polyvinyl alcohol, 60 sulfated polyvinyl alcohol, nitrated polyvinyl alcohol, and the like; partial ethers of polyvinyl alcohol as cyanoethylated polyvinyl alcohol, cellulose, including cotton, viscose, cuprammonium rayon, partial esters of cellulose such as cellulose acetate, cellulose propionate, or cellulose nitrate; partial ethers of cellulose such as methyl cellulose, ethyl cellulose, hydroxy ethyl cellulose, or cyanoethylated cellulose; starch, partial ethers of starch, as for example, cyanoethylated starch; partial esters of starch, as for example, acetylated starch; poly β -hydroxy ethyl methacrylate and copolymers thereof, and poly β -hydroxy ethyl acrylate and copolymers thereof. 75

Among the polymeric ketones which may be used in the practice of the process of the present invention are polyvinyl pyrrolidone, polymethylvinyl ketones, polyethylvinyl ketones, polypropylvinyl ketones and copolymers prepared by polymerizing alkyl vinyl ketones with other polymerizable materials such as those vinylidene and/or vinyl monomers recited hereinabove. 85

The polyamines used in the practice of the process of the present invention are the polyvinyl amines which can be prepared from poly acrylamide and from acrylamide copolymers by treatment with NaOCl by the Hoffman degradation reaction. 90

Example of the polymeric aldehydes which may be used in the practice of the process of the present invention are homopolymers such as polyacrolein, poly 3-butenal, poly 3-pentenal, or poly 5-chloro-3-pentenal, or copolymers prepared by polymerizing acrolein, 3-butenal, 3-pentenal, or 5-chloro-3-pentenal with other polymerizable materials containing the $\text{CH}_2=\text{C}<$ group such as those recited hereinabove. 100

Examples of the polymeric mercaptans which may be used in the practice of the process of the present invention are poly mercaptoethyl acrylate, poly mercaptobutyl acrylate, poly mercaptoethyl methacrylate, poly mercaptopropyl acrylate, or poly mercaptopropyl methacrylate, or copolymers of mercaptoethyl acrylate, mercaptobutyl acrylate, mercaptoethyl methacrylate, mercaptopropyl acrylate, or mercaptopropyl methacrylate with other polymerizable materials containing a polymerizable $\text{CH}_2=\text{C}<$ group as recited hereinabove. 105

Among the acetals which may be used in the practice of the process of the present invention are polyvinyl formal, polyvinyl acetal, or polyvinyl butyral. 115

These reducing agents may be used either singly or in combination with one another. 120

The process of the present invention may be carried out at temperatures between about -5°C .— 100°C . but preferably at temperatures between about 10°C and 60°C .

Temperatures significantly above 70° C. are to be avoided because the redox system sometimes decomposes too rapidly at these temperatures.

5 The process of the present invention may be carried out under pressure or under partial vacuum but it is preferred to utilize atmospheric pressure inasmuch as the reaction runs very favorably at this pressure.

10 When polymerization is carried out in an aqueous media, the pH may be any value up to about 6 and preferably not above 3.5. Extremely low pH values are operable as evidenced by polymerization reactions according to this invention at room temperature as shown in the subsequent examples. The pH value is maintained between 1 and 2 in aqueous polymerization reactions for optimum results.

20 The amount of ceric compound which is utilized in the practice of the process of the present invention may be varied over fairly wide limits. For example, one may utilize from about 10^{-6} to 10^{-10} mole of ceric ion per mole of polymerizable monomer. Preferably, one would use between 10^{-3} to 10^{-2} mole of ceric ion per mole of polymerizable monomer. Ceric ion is preferably introduced into the reaction mixture according to the present invention in the form of a ceric salt. Among the salts adapted for use in the present invention are ceric nitrate, ceric sulfate, ceric ammonium nitrate, ceric ammonium sulfate, ceric ammonium pyrophosphate, or ceric iodate. These compounds may be employed singly or in combination with one another. Ceric compounds which are capable of forming ceric salts *in situ* under the acid conditions of the polymerization reaction such as ceric oxide, ceric hydroxide and the like may be used.

Referring now specifically to the concept of the present invention, related to the grafting of polymer onto a pre-formed polymeric backbone, the number of such grafts on a given backbone may be controlled by controlling the amount of ceric ion added to the reaction mixture. Thus, were a large amount of ceric ion to be added to a given reaction mixture, instead of one such grafted side chain, a number of such chains could be formed, theoretically, at least, at any point on the backbone where the active group of the polymeric reducing agent identified above is found. The length of the polymeric chain is a function of the monomer concentration, ceric ion concentration, temperature and chain transfer constant of the backbone.

55 In general, the times to achieve a desired degree of graft copolymerization may be determined empirically. Thus, for example, a given polymer may be precipitated at different time intervals and the extent of polymerization determined gravimetrically to determine the per cent of the conversion of

monomer to polymer. Where the amount of ceric ion and monomer is known, suitable reaction times may be readily established to achieve the desired degree of polymerization. In addition, the ceric ion when being reduced undergoes a color change from yellow to brown to a substantially colorless state, at which time it is substantially completely reduced and will no longer effectively initiate polymerization. Thus, in an aqueous system or a system which admits of a visual check, an operator is readily able to determine when the reaction has gone to substantial completion.

Should it be desirable to halt the reaction at any given time, while ceric ion is still present in the reaction mixture, this may be done by the addition of hydroquinone, sodium sulfite or ferrous sulfate, which materials exhaust the remaining ceric ion substantially instantaneously, thus halting the reaction. Furthermore, as an additional method of halting the reaction, the pH of the reaction mixture may be adjusted to the alkaline side, as, for example, to a pH of between 7 and 8, to precipitate out the remaining portion of the ceric compound, prohibiting its further reduction, thus stopping the reaction.

The amount of polymeric reducing agent to monomeric material may be varied very extensively depending on the properties of the ultimate product desired. As a consequence, large excesses of either material may be utilized in alternative reactions.

The polymeric reducing agent may be employed in amounts from 1% to 100%, or even more by weight based on the weight of the monomer and preferably from between 10% and 300% by weight based on the weight of the polymerizable monomer.

In order that the concept of the present invention may be more fully understood, the following examples are set forth in which all parts are parts by weight unless otherwise indicated. These examples are set forth primarily for the purpose of illustration and any specific enumeration of detail contained therein should not be interpreted as a limitation of the case except as is indicated in the appended claims.

EXAMPLE 1.

Five parts of acrylamide were added to 100 parts of water containing 5 parts of polyvinyl alcohol (Elvanol 51.05, a commercially available polyvinyl alcohol having a number average molecular weight of 10,000) in a screw cap jar. The solution was then flushed with carbon dioxide and 4 parts of 0.1 N aqueous ceric ammonium nitrate and 4 parts of molar nitric acid were then added. Polymerization was carried out at room temperature (25° C.) for 45 minutes and then the polymer was precipitated by pouring the reaction mixture into an excess of acetone. After

drying for 16 hours at 80° C. in vacuo, a yield of 8.99 parts was obtained which was equivalent to a 79.8% conversion.

- 5 Fractional precipitation of the graft copolymer in a 50:50 by volume methanol-water system was achieved by incremental additions of acetone. This procedure yielded sharp fractions containing from 57 to 60% of polyacrylamide to 43 to 40% of polyvinyl alcohol and some free polyvinyl alcohol. No polyacrylamide was to be obtained.

EXAMPLE 2.

- 15 Five parts of methyl acrylate, inhibitor free, were added to 100 parts of distilled water containing 5 parts of polyvinyl alcohol (Elvanol 51.05). To this solution 10 parts of 0.1 N-aqueous ceric ammonium nitrate containing 1 part of molar nitric acid was added. The reaction container was flushed with carbon dioxide and the polymerization was carried out at room temperature for 75 minutes.

- 25 The resulting latex was poured into an excess of 1:4 hexane-ethanol solution to precipitate the graft polymer. Thereafter, the graft polymer was filtered and dried at 50° C. in vacuo for 16 hours. The yield of graft polymer was 9.62 parts and represented a conversion of 92.4%. The graft polymer was insoluble in acetone and in benzene, although it swelled in both solvents.

- 30 The graft copolymer was not cross-linked because acetylation in a mixture of acetic acid and acetic anhydride at 60° C. brought it into solution. The acetylated graft copolymer was soluble in acetone.

Two parts of the resulting graft polymer upon extraction for 4 hours with boiling acetone suffered a loss in weight of .04 parts. Further extraction in boiling acetone for 20 hours caused an additional loss in weight of .015 parts.

The grafting efficiency of the system, as defined above, was determined by dividing the amount of polymethyl acrylate which was insoluble by the total amount present before extraction. Assuming that the graft is completely insoluble in acetone and that the polymer extracted is pure polymethyl acrylate, the efficiency of the illustrated graft copolymerization of this system was 97%. To further illustrate the difference between graft copolymers and mechanical mixtures, a mechanical mixture containing 1 part of polymethyl acrylate and 1 part of polyvinyl alcohol was extracted for 4 hours in boiling acetone. Under these conditions, 98% of the polymethyl acrylate was extracted.

EXAMPLE 3.

60 Acrylonitrile was steam distilled over 5% phosphoric acid, dried over sodium sulfate and distilled under nitrogen. Three samples of the sizes represented in the table below were then added to aqueous solutions containing the reducing agents set forth in the table below in the proportions reported therein. Ceric ammonium nitrate and nitric acid were then added. The solutions were flushed with carbon dioxide and then polymerized at room temperature for the required period of time.

Ceric Nitrate Moles	Reducing Agent Parts	Acrylonitrile Parts	Water Parts	pH	Time Min.	% Conv.
5×10^{-4}	2.5 PVA *	2.5	50	1	45	85.3
2×10^{-4}	0.5 PVA *	9.5	200	1.5	120	73.8
1×10^{-3}	0.5 Methocel **	9.5	200	1	105	70.1

* Polyvinyl alcohol, Elvanol 51.05.

** Methocel, (A commercially available methyl cellulose having an absolute viscosity of 15 cps. and a methoxy content of 27.5 to 32.0% based on the percentage of hydronyl groups converted to methoxy groups in the preparation of methyl cellulose.). These graft copolymers are insoluble in dimethyl formamide, ethylene carbonate, and concentrated solutions of potassium thiocyanate. The graft copolymers swell up to 100 times their original volume when heated in the presence of dimethyl formamide but when extracted with dimethyl formamide in a Soxhlet Extractor for 24 hours only a very small amount of polyacrylonitrile was found in the solvent.

EXAMPLE 4.

- 75 0.88 part of polyvinyl alcohol (Elvanol 70.05, a commercially available completely hydrolyzed polyvinyl alcohol having an average number of molecular weight of 10,000) was dissolved in 8.8 parts of water. To this solution was added 5.3 parts of acrylonitrile and 80 6.6 parts of N-sodium hydroxide solution.

Cyanoethylation was carried out at 25° C. for 2 hours. The resulting polyvinyl alcohol was 34% cyanoethylated.

The mixture was diluted with 50 parts of water and acidified to pH 1.5 with N-nitric acid and 2×10^{-4} moles of ceric ammonium nitrate were added. Polymerization was carried out at room temperature for 30

minutes. The graft copolymer was filtered and dried in vacuo at 70° C. to yield 5.5 parts of graft copolymer.

The graft was soluble in 60% (by weight) of potassium thiocyanate solution.

EXAMPLE 5.

Five parts of polyvinyl alcohol were dissolved in 100 parts of water in a three neck flask fitted with nitrogen inlet, stirrer and condenser. To this solution was added 22.5 parts of styrene and 5 parts of 0.1 N-ceric sulfate in 1 N-sulfuric acid. The solution was stirred at 40° C. for 30 minutes and then 1 part of Aerosol MA (a sodium dihexyl sulfosuccinate) was added.

Polymerization was carried out for 5 hours at 40° C. The latex was coagulated by pouring into acetone and the polymer was filtered and dried. The total yield of polymer was 22 parts. The polystyrene graft on polyvinyl alcohol was insoluble in benzene.

While the above examples deal generally with the initiation of polymerization and a process for producing graft copolymers and the like, a particularly advantageous facet of the present invention is the application of its principles to a system in which cellulosic materials function as what has been hereinabove referred to as the polymeric reducing agent.

By cellulosic materials hereinabove referred to, fibers, fabrics or paper or other materials composed of cotton, linen, viscose, rayon, wood, paper, or pulp, or mixtures or blends

thereof are intended to be included.

Although the polymerization of olefinic monomers within the fibers of cellulosic materials has been disclosed heretofore, the methods used have several limitations. The most serious of these is the simultaneous polymerization of monomers in the treatment bath and on the surface of the cellulosic material, as well as within the fibers of the material. This results in a waste of monomer as well as an objectionable layer of polymer on the surface of the material which is often difficult to remove. A distinct advantage of this invention is that polymerization can be made to occur substantially entirely within the fibers of the cellulosic material. In addition, the polymer thus deposited is grafted to the cellulose molecules and becomes an integral part of the material.

The following examples are given as a means of illustrating this aspect of the present invention.

EXAMPLE 6.

Five samples of 80×80 cotton percale were treated with aqueous solutions containing varying concentrations of acrylonitrile, ceric ammonium nitrate, and nitric acid. The liquor to fabric ratio was at least 30:1 and the temperature was 30° C. in all instances. Upon completion of the treatment, the fabric was thoroughly washed in order to completely remove traces of nitric acid before drying.

Acrylonitrile Concentration %	Ceric Ion Concentration (molar)	Nitric Acid Concentration (molar)	Time of Treatment (minutes)	Weight Increase of Fabric %
4	0.0002	0.01	30	8.4
4	0.001	0.01	30	18.3
4	0.005	0.05	5	20.3
4	0.005	0.05	10	26.4
7	0.005	0.25	30	39.3

EXAMPLE 7.

A sample of viscose rayon challis, weighing 6.71 parts was treated with 12 parts of acrylonitrile, 15 parts of 0.1 molar ceric ammonium nitrate, 13.5 parts of 1.0 N nitric acid and 256 parts of water for 30 minutes at 30° C. The solution was flushed with carbon dioxide to render it oxygen-free.

The fabric was thoroughly washed after treatment and then dried at 107° C. for 10 minutes prior to weighing. After treatment, washing, and drying, the fabric weighed 8.93 parts, indicating a weight increase of 33.1%.

EXAMPLE 8.

Four samples of 80×80 cotton percale were treated with aqueous solutions containing varying concentrations of acrylamide and fixed concentrations of ceric ion as ceric ammonium nitrate and fixed concentrations of nitric acid, the composition and concentration of the components being given in the table set forth hereinbelow. The liquor to fabric ratio was at least 30:1 and the treatment was continued for 30 minutes at 30° C. in all instances. A carbon dioxide atmosphere was maintained over the polymerization bath at

all times to render it oxygen-free. Upon completion of the treatment, the fabric was thoroughly washed in several changes of water to insure complete removal of nitric acid be-

fore drying. The fabric samples were then dried for 10 minutes at 107° C. before weighing.

Acrylamide Concentration %	Ceric Ion Concentration (molar)	Nitric Acid Concentration (Normal)	Time of Treatment (minutes)	Weight Increase of Fabric %
1.0	0.001	0.01	30	3.9
1.5	0.001	0.01	30	6.5
2.5	0.001	0.01	30	12.5
4.0	0.001	0.01	30	17.6

EXAMPLE 9.

10 A sample of 80×80 cotton percale, weighing 6.26 parts was treated with a solution containing 10 parts of methyl acrylate, 2.5 parts of a 0.1 molar ceric ammonium nitrate in 1.0 N HNO₃, 10 parts of 1.0 N nitric acid and 225 parts of water for 30 minutes at 25° C. A carbon dioxide atmosphere was maintained over the polymerization bath.

15 The final weight of the fabric was 11.85 parts, corresponding to a weight increase of about 88%.

EXAMPLE 10.

A sample of viscose rayon challis, weighing 6.73 parts was treated with a solution consisting of 5 parts of methylene bis acrylamide, 5 parts of 0.1 molar ceric ammonium nitrate in 1N HNO₃, 10 parts of 1 N nitric acid and 230 parts of water for 30 minutes at 30° C. An atmosphere of carbon dioxide was maintained over the polymerization bath.

30 The final weight of the fabric was 7.71 parts, indicating a weight increase of 14.5%.

EXAMPLE 11.

A sample of 80×80 cotton percale was treated according to the procedure described in Example 8 (Sample 2) to deposit polyacrylamide within the fiber of the fabric. The polymer deposit was equal to 7% of the initial weight of the material. The fabric was then treated for 10 minutes with a 37% formalin solution at 85° C. and at a liquor to cloth ratio of 7:1.

After thorough washing to remove excess formaldehyde, and subsequent drying, the fabric was padded through a 3% solution of magnesium chloride catalyst, and then heated to 175° C. for 100 seconds. The wrinkle recovery as determined by the Monsanto wrinkle recovery test method of the treated fabric was 262° compared to 142° for the untreated. The treatment resulted in a tensile strength loss of 32%.

A wrinkle recovery of 250° can be obtained by treating cotton with formaldehyde alone under acid conditions. The tensile strength loss of the treated fabric, however,

is of the order of 70% that of an untreated fabric.

EXAMPLE 12.

A sample of cellulosic filter paper was treated for 5 minutes at 30° C. with a 7% solution of acrylonitrile, 0.005 molar concentration of ceric ion as ceric ammonium nitrate, and 0.05 N nitric acid solution. The solution was flushed with carbon dioxide to render oxygen-free. Thereafter, the sample of filter paper was thoroughly washed with water and dried to give a weight increase of 45%.

The treated paper was cut into small fragments and treated with 200 times its weight of 1.0 molar cupriethylene diamine solution for 20 hours at room temperature. The paper was largely unaffected by the reagent and after washing and drying was found to have lost less than 5% of its weight. The untreated paper subjected to the same solvent action was completely dissolved in less than 6 hours.

The treated paper was then extracted with dimethyl formamide at temperatures of between 70 and 80° C. for 16 hours. The dimethyl formamide remained perfectly clear upon dilution with water, indicating that no free polyacrylonitrile was extracted.

The treated paper showed outstanding resistance to acid and alkali degradation. A sample of paper was immersed for 8 hours in concentrated hydrochloric acid and did not disaggregate or lose its strength. A similar sample remained unchanged when treated for 8 hours with 4% sodium hydroxide at 80° C.

Identical paper samples which have not been treated according to the process set forth above has a tensile strength of 10 pounds when dry and 0 when wet, while paper so treated has a tensile strength of 34 pounds when dry and 28 pounds when wet.

EXAMPLE 13.

Five parts of Carbowax 6000 (a commercially available polyethylene glycol having a molecular weight of about 6,000) was dissolved in 100 parts of water containing 5 parts of acrylonitrile. To this solution was

- added 8×10^{-4} mole of ceric ammonium nitrate and sufficient nitric acid to adjust the pH to 1. The solution was flushed with carbon dioxide and polymerized for 145 minutes at room temperature. The resulting polymer was coagulated, filtered and extracted twice with water at reflux for five hours. The resulting oligo block copolymer contained 89.2% of acrylonitrile and 10.8% Carbowax 6000.
- This example is illustrative of an oligo block copolymer in which the pre-formed polymeric reducing agent (polyethylene glycol) and acrylonitrile are reacted in the presence of a ceric compound. Copolymers of this type may be spun from aqueous potassium thiocyanate and used in the preparation of synthetic fibers.

EXAMPLE 14.

- 15 parts of acrylonitrile and 5 parts of polyvinylamine, prepared from polyacrylamide by Hoffman degradation, were dissolved in 300 parts of water at 25° C. After flushing with nitrogen, the solution was acidified to pH 1.5 with nitric acid and 0.6 part of ceric ammonium nitrate was added. Polymerization started within one minute. After 70 minutes, the polymer dispersion was poured into an excess of acetone and the graft polymer separated by filtration. The yield was 17 parts and represented a 75% conversion of the acrylonitrile.

EXAMPLE 15.

- A mixture of 100 parts of water, 5 parts of Aerosol MA, 40 parts of styrene and 10 parts of acrolein was emulsified by stirring in a suitable reaction vessel. After displacing the air in the vessel with nitrogen, 0.2 part of potassium persulfate were added. Polymerization was carried out for 3.5 hours at 50° C. at which time the conversion of monomer to polymer was approximately 80%. The latex, after stripping the excess monomer under vacuum, contained 23% of styrene-acrolein copolymer.
- 80 parts of the above latex was diluted with 80 parts of water in a reaction vessel equipped with a mechanical stirrer. A solution of 0.5 part of ceric dihexyl sulfosuccinate in 25 parts of ethyl acrylate was added to the emulsion at 30° C. over a period of 1 hour. Upon completion of the addition, the temperature of the reaction mixture was raised to 40° C. and maintained at that temperature for 5 hours. The latex was coagulated with methanol to give 36 parts of graft copolymer, which represented a 70% conversion of the ethyl acrylate.

EXAMPLE 16.

- A solution of 1 part of polyvinyl pyrrolidone and 6.5 parts of acrylonitrile in 100 parts of water was flushed with nitrogen and cooled to 20° C. Two parts of an 0.1 N solution of ceric ammonium nitrate in molar nitric acid were added. Polymerization started immediately. After two hours, the mixture

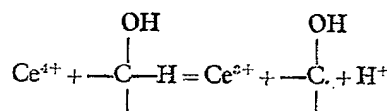
was slurried with 200 parts of acetone and the polymer separated by filtration. The yield was 6.05 part and represented a conversion of 77.5%.

Materials most suitable for the preparation of linear oligo block copolymers are those having a central organic chain which has functional terminal groups such as hydroxy, mercapto, aldehydic, amino, keto, acetal groups, as for example, polyethylene glycol, being generically written as



wherein n is 0 or a positive integer. These compounds range in molecular weight from a few hundred to many thousands, as for example, 4,000 and 6,000 or more. In addition to the above-mentioned materials, the polyethylene imines are also satisfactory for the preparation of the linear oligo block copolymer.

While the detailed mechanism by which the process of this invention operates and the resulting advantages that are produced are not fully known, the ceric ion redox system initiates polymerization of suitable unsaturated monomers through a free radical mechanism according to the following general formula where the polymeric reducing agent is a polymeric alcohol:

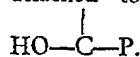


wherein $\text{HO}-\text{C}$ is the free radical capable

of reacting with suitable unsaturated monomers. The oxidation reaction proceeds through a single electron transfer mechanism, the reducing agent donating one electron to the oxidizing agent and the free radical being located on the polymeric organic reducing agent. This is important in that it initiates polymerization on a given reducing agent, i.e., a pre-formed polymeric chain material, at the situs of the carbon atoms having the free radicals thereon, which is believed to be the

carbon atom in the $\text{HO}-\text{C}-\text{H}$ group herein-

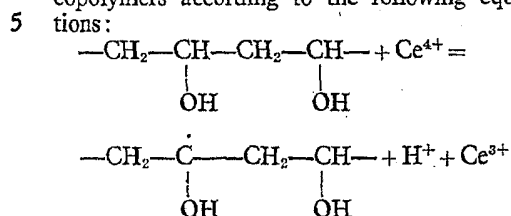
above described. The grafted polymer chain is thus attached to the reducing agent through a carbon linkage, e.g., the polymer P, is attached to the central organic chain as



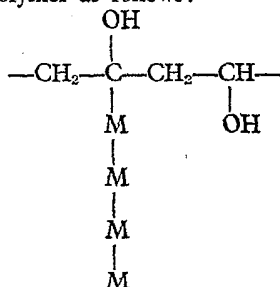
Polymerization of unsaturated monomers in the presence of ceric ion and pre-formed polymer chains or backbones such as cellulose, starch, polyvinyl alcohol, which may

contain a multiplicity of $\text{HO}-\text{C}-\text{H}$ groups

and may therefore be termed polyfunctional reducing agents, are believed to produce graft copolymers according to the following equations:



The free radical on the pre-formed polymer chain (reducing agent) is then believed to react with a given monomer (M) to produce a graft copolymer as follows:



Graft copolymers may, of course, be prepared by conventional methods which take advantage of the chain transfer reaction between growing polymer chains and the backbone. However, the yields of graft copolymers obtained are low and are a function of the degree of conversion. Other methods take advantages of catalysts like persulfates and peroxides, which under certain conditions may attack the backbone to produce free radicals. In these cases, however, a mixture of homopolymers and graft copolymers are obtained, because conventional initiators activate the monomer as well as the backbone.

With ceric salts in the redox system of the present invention, the graft copolymers are substantially free of homopolymers, because the backbones are attacked very rapidly at relatively low temperatures, while the monomers are not.

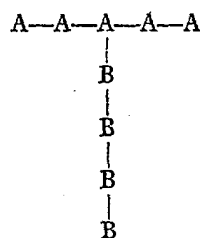
Heretofore, it has been considered impossible to prepare graft copolymers essentially free of homopolymers even with elaborate and impractical processes. The process described herein gives graft copolymers essentially free of homopolymers as one of its major advantages. That is, by this process a substantially pure graft copolymer may be produced.

The advantages of graft copolymers over mixed copolymers is well known. For example, the solvent resistance of graft copolymers is much improved over that of mixtures of polymers. As is shown in Example 12 above, the grafted copolymer of acrylonitrile on cellulose is insoluble in the solvents

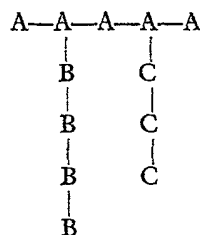
for either poly acrylonitrile or for cellulose.

The absence of free backbone polymer in the polymerization product can be assured by incorporating sufficient ceric salt in the reaction mixture to give at least one reactive site on each backbone molecule. Obviously, the higher the molecular weight of the backbone polymer, the less ceric salt will be required to give this one reactive site per molecule.

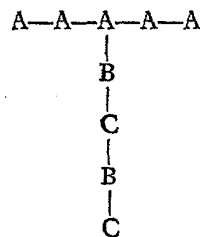
It can readily be seen that the properties of a backbone may be readily and widely varied by employing the process of the present invention. Three types of graft copolymers may be made by this method. First, a homopolymer chain may be grafted to a backbone in accordance with the following general formula wherein A represents a given backbone and B a polymer chain grafted thereon:



Secondly, two different homopolymer chains may be grafted onto a given backbone as by two successive operations of this invention, in accordance with the following general formula wherein A represents a given backbone and B and C different polymer chains grafted thereon:



Thirdly, a copolymer chain can be grafted onto a given backbone, when two suitable monomers are utilized in accordance with the following general formula wherein A represents a given backbone and ---B---C---B--- a given copolymer. In this instance, C may be a monomer which cannot homopolymerize.



By proper selection of monomer or monomers, melting point temperatures, water-proofing characteristics and moldability of a polymer may be suitably modified.

- 5 The next example illustrates how a monomeric material can be grafted onto a graft copolymer.

EXAMPLE 17.

- 10 Into a suitable reaction vessel containing 2.4 parts of a 50—50 graft copolymer of polyvinyl alcohol and polyacrylamide, there is added 4.8 parts of methyl acrylate. The solution is flushed with carbon dioxide and then 4 parts of 0.1 N ceric ammonium nitrate in 15 0.1 N nitric acid are added. The polymerization is carried out for about 1 hour at room temperature (25° C.). The resulting polymeric material is precipitated in an excess of methanol, filtered and dried in vacuo at 50° 20 C. The total yield is 6.75 parts representing a conversion of 94%. The mixed graft copolymer is essentially insoluble in water, acetone and benzene.

- 25 The following example illustrates how two monomeric polymerizable materials may be grafted simultaneously onto a polymeric backbone.

EXAMPLE 18.

- 30 Into a suitable reaction vessel containing 5 parts of polyvinyl alcohol (Elvanol 51.05) dissolved in 100 parts of distilled water, there is added 5 parts of acrylamide, 5 parts of methyl acrylate and 4 parts of 0.1 N ceric ammonium nitrate in 1.0 N nitric acid. Copolymerization is carried out for 20 minutes 35 at room temperature. The resulting suspension is precipitated with an excess of ethanol. The graft copolymer thus produced is filtered and dried in vacuo at 70° C. The total yield 40 is 14.8 parts. The graft copolymer thus produced is insoluble in acetone but is easily dispersible in water.

- 45 Several methods of preparation of block copolymers have been described heretofore. Their synthesis requires the preparation of individual block polymers containing reactive groups at both ends and a subsequent joining of these blocks through a second step. Most 50 second steps involve the condensation of these pre-formed blocks.

- When unsaturated monomers are polymerized in the presence of ceric ions and suitable reducing agents, such as trimethylene glycol, 1,4-butanediol and the like polymer 55 molecules containing hydroxyl groups on one or both ends, depending upon the termination reaction, are believed to be formed. These polymers can then be reacted further as a polymeric reducing agent with another 60 monomer in the presence of ceric ions to produce a copolymer consisting of a few long sequences of the two monomers. These linear oligo block copolymers are substantially different from the block copolymers previously 65 described because the physical prop-

erties of a block copolymer are a function of the length and number of sequences.

Copolymers prepared from hydrophobic and hydrophilic blocks show peculiar solubility characteristics and can be used as surface active agents. Graft copolymers can also be used as adhesives and bonding agents for non-woven fabrics and for pigments.

70 It will be noted in the above examples, and particularly with regard to Examples 7—12 relative to the graft polymerization of suitable monomers on the cellulosic backbones of materials such as cotton fabric, regenerated cellulose fabric, viscose rayon fabric, paper, paper pulp, wood, or wood pulp, that certain 80 advantages of the present process, namely, its ability to operate at low temperatures, and more specifically room temperature, and the fact that excessive loss of monomer due to homopolymerization in the bath are obviated. 85 This is particularly evident with regard to Example 12, wherein the graft polymer was insoluble in both cupri-diethylene diamine and dimethyl formamide, indicating that the cellulose molecule was modified and that no free polyacrylonitrile was present. This is believed to indicate clearly that the polyacrylonitrile is grafted onto the cellulosic 90 backbones of the material.

By employing the process of the present invention, wherein the reducing agent is cellulose or cellulosic materials, the properties of said materials may be varied to impart greater utility heretofore unobtainable. By the 95 process of the present invention, new finishes for fibers may be obtained, dyes and finishes may be rendered more durable on both fabric and paper. Surface characteristics of metals may be modified, now rubber-soluble 100 polymers may be produced, new modifiers, additives and plasticizers for plastics and resins may be produced. Pigment of improved bleed resistance and new pigment bonding agents may be produced. Protein and 105 proteinaceous materials may be modified to improve existing properties or to impart new properties thereto. With regard to textiles and textile materials, in addition to providing a means of preparing more durable finishes and new finishes for fabrics, fibers and fabric may 110 be rendered more resistant to fire, shrinkage, rot, acids, mildew, and the like. In addition, their tensile strength and wrinkle resistance, and the like may be improved.

With suitable reducing agents, new classes 120 of surface active agents may be readily prepared. Thus, for example, polymers possessing hydrophilic characteristics may be readily grafted onto a suitable backbone, as, for example, at a second point thereon. In addition, 125 new lubricating oil additives may be developed and properties of existing ones improved. In many instances, the polymerization products of the present invention may be further co-reacted with various resins, includ- 130

ing amino resins, such as urea-formaldehyde condensates, triazine formaldehyde condensates of various ethylene ureas, or the alkylated derivatives of these materials to achieve a wide variety of desired end properties, particularly in the fields of textile and paper chemistry.

The above-enumerated potential uses of the concepts of the present invention are only a relatively few of the many which will readily occur to those skilled in various arts.

In practice of the process of the present invention, when an aqueous emulsion technique is used, one will choose to make use of an emulsifying agent of which there are many known in the art. Inasmuch as the process of the present invention including the aqueous emulsion processes are carried out at pH values not greater than 6.0, it is preferred to make use of those emulsifying agents which do not tend to precipitate from an acid medium, particularly, one within the pH range of operation. Among the emulsifying agents which may be used in the process of the present invention, are the sodium dialkyl sulfosuccinates such as the sodium diisobutyl sulfosuccinate, sodium diamyl sulfosuccinate, sodium dihexyl sulfosuccinate, sodium dioctyl sulfosuccinate, or sodium ditiodecyl sulfosuccinate, or one may use the sodium alkyl, aryl sulfonates such as sodium octyl benzene sulfonate, sodium decyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium octadecyl benzene sulfonate, or sodium isopropyl naphthalene sulfonate. Additionally, one may use the sodium alkyl sulfates such as sodium lauryl sulfate or sulfonated mineral oils may be used. The salts other than the sodium may be used; for instance, the potassium salts, the lithium salts and the like. Quite obviously, these emulsifying agents may be used either singly or in combination with one another. The amount of emulsifying agent used will depend in some measure on the degree of water insolubility of the components used in the reaction, namely, the vinylidene monomer, the polymeric reducing agent and the ceric salt. At any rate, the amounts conventionally used as a range will find adequate application in the practice of the present invention.

In the practice of the present invention, one may make use of inorganic ceric salts or organic ceric salts such as the oil soluble ceric salts. Certain of the latter have been used in some of the examples set forth hereinabove such as Example 15. For the purposes of this invention, these oil soluble ceric salts may be formed in situ or they may be used as a preformed oil soluble ceric salt. In order to prepare these oil soluble ceric salts, one reacts an inorganic ceric salt such as ceric ammonium nitrate with an organic sulfur containing acid. These organic sulfur containing acids may be either monobasic or polybasic, saturated or

unsaturated, aliphatic or aromatic. Illustrative of these acids are the following: The mono and disulfosuccinic acids, sulfochlor-succinic acid, sulfoadipic acid, sulfopyro-tartaric acid, sulfoglutaric acid, sulfosuber-ic acid, sulfosebacic acid, sulfomaleic acid, sulfofumaric acid, sulfodimethyl succinic acid, sulfomethylglutaric acid, sulfopol-melinic acid, sulfopropylsuccinic acid, or sulfooctylglutaric acid. Still further, the alkyl esters of these sulfocar-b-oxylic acids such as the methyl, ethyl, propyl, butyl, amyl, hexyl, octyl esters may be used. Additionally, one may make use of the monoalkyl esters of sulfuric acid such as monobutyl acid sulfate, monoamyl acid sulfate, monooctyl acid sulfate, or mono-lauryl acid sulfate. Additionally, one may make use of the alkyl benzene sulfonates such as the octyl benzene sulfonate, nonyl benzene sulfonate, decyl benzene sulfonate, dodecyl benzene sulfonate, octadecyl benzene sulfonate, or isopropyl naphthalene sulfonate. These organic sulfur-containing acid materials are preferably used as alkali metal salts in reaction with the ceric ammonium nitrate to form the organic oil soluble ceric salts. The preferred alkali metal is sodium although others such as potassium, lithium and the like may be used.

When the ceric ammonium nitrate and the sodium salt of the organic sulfur-containing acid are blended together in aqueous solution, the ceric salt or complex of the organic sulfur-containing acid is formed, and being insoluble in water, it precipitates from solution and can readily be collected by ordinary filtration or other mechanical means such as centrifugation and the like. The concentration of either component in solution is not critical and, as a consequence, relatively small amounts such as 1% or more may be used. The preferred concentration of either component in solution will be about 10 to 15%, although higher concentrations may readily be used.

The reaction may be carried out at a temperature between about 0° C. and 50° C. but preferably between about 10° C. and 30° C. There is no need ordinarily to endeavor to control the pH inasmuch as the reactants themselves will ordinarily cause the pH to be around 3 or below. In the event, however, that the pH is not low enough, it may be adjusted by adding a sufficient amount of an acid material. One should make sure that the pH is sufficiently low so that no hydrolysis takes place in the course of the preparation of the oil soluble ceric salt.

Due to the characteristics of the ceric ion, the ultimate oil soluble ceric product may be classed as a salt or as a complex.

Among the oil soluble ceric salts which may be produced in accordance with the process outlined hereinabove are ceric dihexyl sulfo-

succinate, ceric dioctyl sulfosuccinate, ceric diheptyl sulfoglutarate, ceric didecyl sulfosuberate, ceric dilauryl sulfosuccinate, ceric dimethyl sulfomaleate, ceric dimethyl sulfofumarate, ceric dibutyl sulfodimethylsuccinate, ceric dilauryl sulfomethylglutarate and comparable ceric salts which can be produced by reacting any of the sodium salts of the organic sulfur containing acid compounds listed hereinabove with ceric ammonium nitrate.

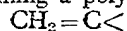
In order that the process of preparing these oil soluble ceric salts be more completely understood, the following example is set forth in which all parts are parts by weight unless otherwise indicated. This example is set forth primarily for the purpose of illustration.

PROCESS FOR THE PREPARATION OF CERIC DIHEXYL SULFOSUCCINATE.

Into a suitable reaction vessel equipped with a mechanical stirrer, there is introduced a solution of 11 parts of ceric ammonium nitrate in 100 parts of water at room temperature. With constant stirring, there is added thereto a solution of 15.4 parts of sodium dihexyl sulfosuccinate in 100 parts of water. The stirring is continued even after the addition is completed and is stopped only when all of the precipitate has come out of the blended solutions. The precipitate is separated from the water by a simple filtration producing a yield of 14 parts of ceric dihexyl sulfosuccinate.

WHAT WE CLAIM IS:—

1. A process for preparing graft polymers and linear oligo block copolymers comprising polymerizing a polymerizable monomeric compound containing a polymerizable



group in an aqueous medium at a pH not greater than 6.0 and at a temperature between -5°C . and 100°C . in the presence of a ceric salt which is soluble in at least one of the components of the reaction system, and a polymeric organic reducing agent which is capable of being oxidized by said ceric salt and which is capable of initiating the polymerization, said agent being an aldehyde or an acetal or a compound containing the

$\begin{array}{c} \text{X} \\ | \\ -\text{C}-\text{H} \\ | \end{array}$ group wherein X is OH, RCO, SH

and NH₂R, wherein R is hydrogen, alkyl, aralkyl or aryl, the open bonds of said

$\begin{array}{c} \text{X} \\ | \\ -\text{C}-\text{H} \\ | \end{array}$ group being essentially organic residues and/or hydrogen.

2. A process according to claim 1, in which the polymerization is carried out at a pH not greater than 3.5.

3. A process according to claim 1 or 2, in which the monomeric compound is dissolved at least partially in the aqueous medium.

4. A process according to any one of the preceding claims, in which the monomeric compound is polymerized in an aqueous emulsion.

5. A process according to any one of claims 1 to 4, in which the reducing agent is a polyvinyl alcohol.

6. A process according to any one of claims 1 to 4, in which the reducing agent is a polymeric aldehyde comprising the copolymer of acrolein and a polymerizable monomeric compound containing a polymerizable $\text{CH}_2=\text{C}<$ group.

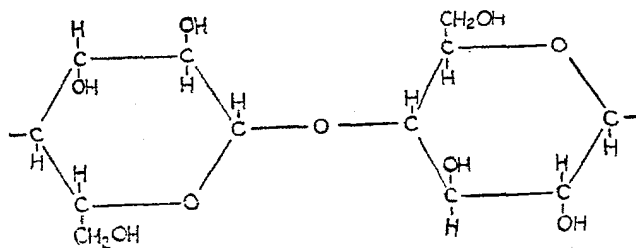
7. A process according to claim 6, which comprises polymerizing, ethyl acrylate in the presence of a polymeric aldehyde comprising a copolymer of acrolein and styrene.

8. A process according to any one of claims 1 to 4, in which the monomeric compound is acrylonitrile and the reducing agent is polyvinyl pyrrolidone.

9. A process according to any of claims 1 to 4, in which the monomeric compound is acrylonitrile and the reducing agent is polyvinyl amine.

10. A process according to claim 5, in which the monomeric compound is styrene.

11. A process for preparing graft polymers comprising polymerizing a polymerizable monomeric compound containing a polymerizable $\text{CH}_2=\text{C}<$ group dissolved at least partially in an aqueous medium at a pH not greater than 3.5 in the presence of a ceric salt which is soluble in at least one of the components of the reaction system and a cellulosic material which is capable of being oxidized by said ceric salt and which is capable of initiating the polymerization, said cellulosic material containing the recurring



or a partial ether or partial ester thereof.

12. A process according to claim 11, in which the cellulosic material is cellulose.

5 13. A process according to claim 11, in which the cellulosic material is cotton.

14. A process according to claim 13, in which the monomeric compound is acrylonitrile.

15. A process for preparing graft polymers

substantially as hereinbefore described with 10 reference to the Examples.

16. A graft polymer whenever prepared by the process according to any one of the preceding claims.

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